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IS : 7444 - 1974
(Reaffirmed 2002)

Indian Standard
CODE OF SEFETY FOR METHANOL

(Second Reprint OCTOBER 1997)

UDC 661.721 : 614.878

भारतीय मानक ब्यूरो
Bureau of Indian Standards
Intranet Print
नई दिल्ली/New Delhi

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BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

Gr 4 *March* 1975

Indian Standard

CODE OF SAFETY FOR METHANOL

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(*Continued on page* 2)

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(*Continued on page* 15)

Indian Standard

CODE OF SAFETY FOR METHANOL

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 1 October 1974, after the draft finalized by the Chemical Hazards Sectional Committee had been approved by the Chemical Division Council.

0.2 Methanol (CH_3OH), also known as methyl alcohol and carbinol, is a clear colourless mobile liquid. It possesses distinct narcotic properties. Its main toxic effect is exerted upon the nervous system. It is a dangerous fire hazard when exposed to heat or flame.

0.3 For proper utilization of a code of safety, a knowledge of effects of hazardous substances on biological systems is desirable.

0.4 The properties of methanol listed under **3** have been taken from literature and have been included for information only. Moreover, these properties pertain to pure methanol. However, for technical methanol, IS : 517-1967* has been published.

0.5 In the preparation of this code, assistance has been drawn from Chemical Safety Data Sheet No. SD-22 'Methanol' issued by the Manufacturing Chemists' Association, USA.

1. SCOPE

1.1 This standard describes properties of methanol, the nature of hazards associated with it and essential information on storage, handling, packing, labelling, disposal of waste, cleaning and repair of containers, selection and training of personnel, personal protective equipment and first aid.

1.2 Attention of the users of this code is directed to the fact that the production, storage, transport, import and export of methanol in India is controlled by the Chief Controller of Explosives of the Government of India under *The Inflammable Substances Act, 1952.* The statutory regulations are embodied in the Petroleum Rules, 1937 issued by the Government of India.

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*Specification for methanol (methyl alcohol) (*first revision*).

2. TERMINOLOGY

2.1 For the purpose of this standard, definitions given in IS : 4155-1966* and IS : 4167-1966† shall apply.

3. PROPERTIES OF METHANOL

3.1 The important properties of methanol are as follows :

a)	Colour	Colourless, water white
b)	Boiling point	64·5°C at 760 mmHg
c)	Density (g/ml)	0·791 3 at 20°C
d)	Hygroscopicity	None
e)	Odour	Pure material has a slight alcoholic odour. Other grades may have a pungent oily odour
f)	Flash point:	
	Open cup	16°C
	Close cup	12°C
g)	Reactivity	Not dangerously reactive
h)	Solubility	Miscible in all proportions with water
j)	Corrosivity	Slightly corrosive to metals especially in presence of moisture. Exceptions—lead and aluminium
k)	Freezing point	−97·6°C
m)	Vapour density (air = 1)	1·11
n)	Flammable limits, percent by volume in air at STP	7·3 to 36
p)	Vapour pressure	at 0°C — 52 mmHg at 20°C — 96 mmHg at 40°C — 253 mmHg
q)	Auto-ignition Temperature	470°C
r)	Refractive index at 20°C	1·331 2
s)	Latent heat of vaporization	262·8 cal/g at 64·7°C
t)	Latent heat of fusion	16·4 cal/g at −97°C

4. HAZARDS ASSOCIATED WITH METHANOL

4.1 Health Hazards — Methanol is harmful by inhalation of the vapour and by prolonged or repeated contact of liquid or vapour with the skin. The effects may be cumulative. It is highly toxic when taken orally.

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*Glossary of terms relating to chemical and radiation hazards and hazardous chemicals.

†Glossary of terms relating to air pollution.

4.1.1 *Threshold Limit Value (TLV)* in Air* — The upper limit of vapour concentration considered safe for continuous exposure for 8 hours work day and 40 hours work week is 200 ppm (262 mg/m^3).

4.1.2 *Acute Toxicity*

4.1.2.1 Methanol is readily absorbed from the gastro-intestinal tract. A dose of as little as 30 to 100 grams by mouth may be fatal to man or pose a threat of serious toxicity. Initial symptoms vary according to the dose and consist of weakness and fatigue, dizziness, headache, nausea, gastro-intestinal disturbances and some degree of inebriation.

4.1.2.2 The initial phase is usually followed by a period during which the individual has very few symptoms. After a latent period of six to thirty hours, the initial symptoms recur with increased severity and profound illness may develop with associated visual disturbances, shortness of breath, abdominal pain and diarrhoea. The patient becomes weak, apathetic and comatose or he may become excited, maniacal and suffer from hallucination. In nonlethal cases of methanol poisoning, recovery is very slow and is accompanied by symptoms of malaise and painful extremities. This is a consequence of the gradual oxidation of methanol to formic acid. This acid accumulates and markedly depletes the alkali reserve of the body.

4.1.2.3 The most characteristic feature of severe methanol poisoning is visual disturbance. However, if the patient recovers, partial or total blindness may persist for some time or be permanent. The visual disturbance results from metabolic formation of formaldehyde within the optic tissues.

4.1.2.4 Inhalation of methanol vapour at high concentrations may irritate the mucous membranes of the respiratory tract and cause mild symptoms of systemic toxicity. Profound or fatal narcosis can occur after exposure of one or two hours at concentration of the order of 50 000 parts per million. Atmospheric concentrations shall be maintained at all times at levels not exceeding 200 ppm.

4.1.2.5 Repeated or prolonged contact of methanol liquid or vapour with the skin causes defatting, drying, brittleness, cracking and irritation. Absorption from prolonged or massive skin contact can lead to serious poisoning and possibly to death, although evidence of the latter is not established clearly.

4.1.2.6 High concentrations of vapour, mist or liquid contacting the eye surface are irritating and cause lachrymation and a burning sensation.

4.1.3 *Chronic Toxicity* — Repeated exposures by any route or absorption may cause systemic poisoning including varying degrees of temporary or permanent visual impairment.

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*As accepted by the American Conference of Governmental Industrial Hygienists, USA.

4.2 Fire Hazard

4.2.1 Methanol is a flammable liquid, and as such introduces a potential fire hazard wherever it is stored, handled or used.

4.2.2 At ordinary temperatures methanol gives off vapour which when mixed with air is explosive within certain limits (*see* **3.1**).

4.2.3 Carbon dioxide or dry chemicals are considered most effective hand extinguishers for fires involving methanol. Water spray can also be used, but water in a straight hose stream should not be used, as this tends to scatter the liquid and spread the fire. Automatic sprinklers and hose lines with spray are recommended for general fire control. Automatic carbon dioxide or dry chemical systems are effective for extinguishment. The application of the proper type of fire protection methods can be best determined by experienced fire protection personnel. Larger spills or tank fires are best controlled with 'alcohol type' foam.

4.2.3.1 Firemen fighting fires of methanol should use necessary protective equipment and breathing apparatus as would normally be used when fighting fires where there may be danger of breathing hazardous products of combustion.

5. HANDLING AND STORAGE

5.1 Methanol is classified as a flammable liquid and hence when it is shipped by rail, water or highway, it shall be packed in authorized containers.

5.2 Methanol is usually transported in steel drums or in tank cars or trucks, and also in glass bottles or metal cans (4·5 litres *maximum*) enclosed in wooden boxes. Lead-lined or aluminium containers are more resistant.

5.3 Tank cars shall bear the placard marked 'DANGEROUS' and the motor vehicles carrying 500 kg or more gross mass of methanol shall be marked 'FLAMMABLE'.

5.4 Bulk Storage

5.4.1 On storage tanks, lightning conductors shall be installed.

5.4.2 'Danger' and 'No Smoking' signs have to be posted at the tank and the store house.

5.4.3 Every tank shall be earthed to prevent static electricity from accumulating.

5.4.4 Every tank shall be tightly sealed and should be provided with vent pipes and flame arrester.

5.4.5 Around storage tanks, dykes shall be built to keep the liquid from flowing out in case of damage to the tank.

5.5 Wherever methanol is being handled, the area shall be posted with 'No Smoking' signs. If leaks or spills occur, the container shall be removed outdoors or to isolated, well-ventilated area and the contents transferred to other suitable containers. All spills should be flushed away promptly with water. Large quantity of methanol shall not ordinarily be permitted to enter drains or sewers where there is danger of vapour becoming ignited. Rail road locomotives and automotive equipment, and equipment capable of causing ignitions, shall be excluded from the area during both unloading and loading operations.

5.6 Storage and Handling of Small Containers

5.6.1 The storage and handling of methanol in glass containers is not recommended except in small amounts for laboratory use. Safety cans with flowing outlet equipped with tight fitting caps or valves shall be used.

5.6.2 All indoor storage areas should be provided with automatic sprinklers.

5.6.3 Before drums are opened they shall be supported and grounded. The methanol drum shall also be bonded to the container or equipment to which the methanol is to be transferred.

5.6.3.1 Drums shall be opened with care and fittings shall never be struck with tools or other hard objects which may cause sparking. To remove the body plug from the drum of the methanol the operator shall wear goggles and use a bung or plug wrench. He shall place the bung up, stand to the side, and face away during operation. After the plug starts to loosen, it shall not be given more than one full turn. If internal pressure exists it shall be allowed to escape to the atmosphere. Then only the operator shall loosen the plug further and remove it. The preferable safe method for emptying drums is by hand pump or electrical pumps with explosion-proof motors. Air pressure shall not be used for emptying drums.

5.6.4 *Tank Trucks*

5.6.4.1 The loading operation shall be carried out by reliable and properly instructed operator in cooperation with the driver.

5.6.4.2 Before unloading the truck, engine shall be stopped and shall not be started during the entire unloading operation.

5.6.4.3 Truck brakes shall be set and as an additional precaution, the wheels shall be blocked. Before any connection or contact is made between the tank truck and the unloading line or other unloading equipment the tank truck should be electrically grounded. All containers to be filled from the truck shall be bonded (electrically connected) and grounded to the truck before filling operations are started. It is preferable to have the truck loading facilities by level and paved. Air pressure shall never be used for unloading tank trucks of methanol.

5.6.5 *Tank Cars*

5.6.5.1 Because of the flammable properties of methanol, the unloading of tank cars containing methanol requires careful operations. It is

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considered good practice to place derails at one or both ends of the unloading tracks approximately one car length from the car being unloaded unless the car is protected by a closed and locked switch or gate. Caution sign shall be so placed on the track or on the car as to give necessary warning to persons approaching the car from open end or ends of siding and shall be kept till the car is unloaded and disconnected.

5.6.5.2 Car number shall be compared with the one on the shipping papers or invoice to verify contents of car to avoid mixing of products. All tools and implements used in unloading car shall be kept away from oil, dirt and grit.

5.6.5.3 Before manhole cover or outlet valve is removed, tank car shall be relieved of all internal pressure. This can be done by opening vent valve or partially releasing the bolting on the manhole cover.

5.6.5.4 Before any connection or contact is made between the tank car and unloading line or other unloading equipment, the tank car shall be grounded in an effective manner.

5.6.5.5 Tank cars may be unloaded through either the top or the bottom outlet. When unloading through bottom outlet, special precautions shall be taken. Air pressure shall never be used for unloading tank cars for methanol. Use of a pump is the recommended method. The air should be vented during unloading.

5.6.5.6 If it is necessary to discontinue the unloading of a tank car, all unloading connections shall be disconnected. All valves shall first be tightly closed and the washer of all other components securely applied.

5.6.6 *Storage* — When the filled drums or other containers are stored indoors, they shall be stored in non-combustible, well-ventilated structures. Drum storage areas should be separated from other areas with approved fire doors. All storage areas shall be provided with automatic sprinklers or other suitable extinguishing system. Other combustibles, acids or oxidizing materials shall not be stored nearby. Drums stored outdoors shall be protected from the direct rays of the sun.

6. PACKING AND LABELLING

6.1 Packing

6.1.1 The material shall be packed in suitable drums conforming to IS : 2552-1970*

6.1.2 Each container shall be securely closed and shall bear legibly and indelibly the following information :

a) Name of the material,
b) Name of the manufacturer,
c) The word 'POISON', and
d) Fire hazard.

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*Specification for steel drums (galvanized and ungalvanized) (*first revision*).

6.1.3 Rail tanker and road tanker shall be sealed after filling in order to avoid tampering on the way.

6.2 Labelling

6.2.1 Each container (including tank cars) shall carry an identifying label or stencil.

6.2.2 Each container shall also bear the relevant label as depicted in IS : 1260 (Part I)-1973*. The following label test shall be included in the lower half of the label, in addition to or in combination with any label warning or other statements required by statutes, regulations or ordinances :

> METHANOL
>
> DANGER ! POISON ! HIGHLY FLAMMABLE !
>
> Keep away from heat; sparks and open flame.
> Avoid contact with eyes.
> Harmful if inhaled.
> May be fatal or cause blindness if swallowed.

7. PREVENTIVE MEASURES

7.1 Employee Education and Training — Safety in handling methanol depends to a great extent upon the effectiveness of employee education, proper safety instructions, intelligent supervision and the use of safe equipment. Training classes for both new and old employees should be conducted periodically to maintain a high degree of safety in handling procedures and employees should be informed of the hazards that may result from improper handling. They shall be cautioned to prevent spillages and told the action to take in case they occur. All the employees shall be fully informed about the first aid measures and what to do in case of emergency. In addition, the employees' training shall include the following:

a) Instructions and periodic drills or quiz regarding the locations, purpose and use of emergency fire fighting equipment, fire alarms and emergency shut down equipment, such as valves and switches and personal protective equipment.
b) Inspections and periodic drill or quiz regarding the location of safety showers, eye baths or the closest source of water for use in emergencies.
c) Instructions to avoid unnecessary inhalation of vapour of methanol and direct contact with the liquid.
d) Instructions to report to proper authority all signs of illness, and all cases of equipment failure.

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*Pictorial markings for handling and labelling of goods: Part I Dangerous goods.

7.2 Personal Protective Equipment — The correct usage of personal protective equipment requires education of the worker in proper employment of the equipment available to him. The following personal protective equipment shall be used when indicated.

7.2.1 *Eye Protection*

7.2.1.1 *Chemical safety goggles* — Cup type or rubber framed goggles equipped with approved impact resistance glass or plastic lens shall be worn whenever there is danger of methanol coming in contact with eyes. Goggles shall be carefully fitted by adjusting the nose piece and head band to ensure maximum protection and comfort.

7.2.1.2 *Spectacle type safety goggles* — Metal or plastic rim safety goggles with side shields which can be obtained with a safety lens or all-plastic safety goggles may be used where continuous eye protection is desirable as in laboratories. These types, however, shall not be used where complete eye protection against methanol is needed.

7.2.1.3 *Face shields* — Plastic shields (full length, 20 mm minimum) with forehead protection may be worn in addition to chemical safety goggles where complete face protection is desirable. Chemical safety goggles shall always be worn as added protection, where there is danger of materials striking the eyes from underneath or around the sides of the face shields.

7.2.2 *Respiratory Protection* — Severe exposure to methanol may occur in tanks during cleaning and repairs or due to spillages or in case of failure of piping or equipment. Employees who may be subjected to such exposures shall be provided with proper respiratory protection and trained in its use and care. Respiratory protective equipment shall be carefully maintained, inspected, cleaned and sterilized at regular intervals and always before and after use by another person. Available types are described in **7.2.2.1** to **7.2.2.4**.

7.2.2.1 *Self-contained breathing apparatus* — This permits the bearer to carry supply of air compressed in the cylinders or self-generating type which produces oxygen chemically. These allow considerable mobility. The length of time a self-contained breathing apparatus provides protection varies according to the amount of air or regenerating material it carries.

7.2.2.2 *Positive pressure hose masks* — These masks are supplied air by blowers and require no internal lubrication. The wearer shall be able to use the same route for exit as for entrance and shall take precautions to get the hose line free from entanglement. The air blower shall be placed in an area free of contaminants.

7.2.2.3 *Air line masks* — These masks are supplied with cleaned compressed air, suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply. These masks are usually supplied with air piped to the area from a compressor. It is extremely important that the air supply is taken from a safe source and that it is not contaminated by oil decomposition from inadequate cooling at the compressor. The safer method is to use a separate, non-lubricated compressor. Pressure reducing and relief valves as well as suitable traps and filters shall be installed at all mask stations. An alternative arrangement frequently used is high pressure breathing air from standard (5·66 m^3) cylinders with a demand type valve and face piece.

7.2.2.4 *Industrial canister type gas masks* — It shall be equipped with full face piece and fitted with an appropriate canister for absorbing vapour. These will afford protection against concentrations not exceeding 2 percent by volume when used in accordance with manufacturer's instructions. The oxygen content of the air shall not be less than 16 percent by volume. The masks shall be used for relatively short exposure periods only. They may not be suitable for use in an emergency since at that time the actual vapour concentration is unknown, and an oxygen deficiency may exist. The wearer shall be warned to leave the contaminated area immediately on detecting the odour of harmful vapour. This may indicate that the mask is not functioning properly, or that the vapour concentration is too high, or that the canister is exhausted or that the mask is not properly fitted.

7.2.3 *Head Protection* — Safety helmets shall be worn where there is danger from falling objects. If safety helmets are not considered necessary, any other hats or caps which are not affected by methanol may be worn to give protection against liquid leaks and splashes.

7.2.4 *Foot Protection* — Leather or rubber shoes with built-in steel toe caps are recommended for workers handling drums and cans of methanol. Rubbers may be worn over leather safety shoes. Rubbers and shoes shall be thoroughly cleaned and ventilated after contamination.

7.2.5 *Body, Skin and Eye Protection* — Sustained or intermittent skin contact with liquid methanol produces dermatitis at the site of contact. Absorption from prolonged skin contact can lead to serious poisoning. It is essential that contaminated clothing be removed, washed and thoroughly dried before using. Affected areas of the body shall be washed thoroughly with soap and water (except the eyes). As a general hygienic measure, facilities for personal cleanliness shall be provided and washing before lunch and at the end of the day shall be encouraged. Clothing made of rubber or other impervious material may be worn to protect the body against methanol splashes.

8. PREVENTIVE MEASURES

8.0 The most important factor in prevention of injury from methanol is avoidance of oral intake and prolonged breathing of vapours.

8.1 Environmental Control — Methanol constitutes a serious industrial hazard if workers are not adequately instructed in proper working and handling techniques. It shall be made clear that this is not a form of alcohol for drinking. Supplies of methanol shall be labelled as poisonous and secured from access of unauthorized persons. Contact with the skin and eyes as well as inhalation of vapour shall be avoided.

8.2 Personal Hygiene — Employees shall be instructed to report any signs or symptoms of change in health and to obtain medical attention. Contaminated items of clothing should be removed to preclude continued skin contact.

8.3 Physical Examination

8.3.1 *Preplacement Physical Examination* — It is desirable to exclude from potential exposure to methanol, prospective employees with the following conditions :

a) Neurologic disturbances or behavioural abnormalities,
b) Alcoholism,
c) Skin disorders, and
d) Eye complaint.

8.3.2 *Suggestions to Physicians* — All individuals suspected of having ingested or severely exposed to methanol shall be kept under observation due to its delayed effects. Characteristically, the onset of severe symptoms is encountered after six to thirty hours latent period. The treatment consists of the following measures :

a) Gastric lavage, if orally ingested.
b) Whisky (or 50 percent ethyl alcohol-water) is given 30 ml every 3 to 4 hours by mouth or stomach tube until 24 hours after the manifestations of poisoning subsided. A blood level for ethyl alcohol of 0·1 percent shall be maintained throughout the course of treatment.
c) Sodium bicarbonate is given by mouth or stomach tube in 5 to 10 g every 15 minutes to an hour as required. It is essential to continue giving alkali as long as any danger of the return of acidosis exists. This is accomplished by frequently checking the plasma carbon dioxide combining power.
d) *Hemodialysis* — Especially in severe cases it is reported as being highly effective.

9. FIRST AID

9.1 General Procedures — Methanol is highly poisonous if taken internally, or when there is heavy exposure by inhalation or skin contact. Remove the individual from the area at once and seek medical attention. Do not give anything by mouth to an unconscious patient.

9.2 Contact with Skin — Remove contaminated clothing and cleanse skin with soap and water. Although prolonged or repeated contacts may be damaging to the skin, acute systemic illness will rarely be seen as a result of skin contact.

9.3 Contact with Eyes — If methanol is splashed into the eyes, irrigate for at least 15 minutes liberally with water and obtain medical attention.

9.4 Taken Internally — Methanol taken by mouth poses serious threat to life and requires intensive medical care. If an individual has swallowed methanol and is conscious, vomitting shall be induced by having him insert a finger down his throat or by drinking luke warm salty or soapy water. Call a physician promptly. Irrespective of the quantity swallowed, insist that the individual remain under close medical care and observation for several days.

10. TANK AND EQUIPMENT CLEANING AND REPAIRS

10.1 Tank and equipment cleaning shall be under the direction of trained personnel who are familiar with all the hazards and safeguards necessary for the safe performance of the work.

10.2 Tanks and equipment, pumps, piping and valves shall always be drained and thoroughly flushed with water before being repaired. No repair job shall be taken up while the equipment is in operation and the lines are full of methanol. It shall be ascertained that all sources of ignition have been eliminated from the vicinity of the tank car. All pipe lines to the tank shall be disconnected and all connecting lines shall be blanked off. The tank may be steamed to remove residual methanol vapours. After this, the tank shall be cooled preferably by filling with water and draining once or twice. Inside atmosphere air shall be tested for oxygen and methanol vapour before permitting personnel to enter. The steam and water lines shall be electrically bonded to prevent the accumulation of static electricity.

10.2.1 None should enter a tank or a confined space until a work permit has been signed by an authorized person indicating that the air has been tested and found to be safe. When a man enters the tank, one man on the outside of the tank shall keep the man in the tank under observation and another man should be available nearby to aid if the man in the tank is overcome.

10.2.2 A supplied air respirator or a self-contained breathing apparatus together with rescue harness and life line shall always be located outside the tank entrance for rescue purposes, regardless of the type of equipment or air supply which is provided for the man inside the tank.

10.3 Exterior Repair Work — Exterior tank repair including repairs to steam coils, cutting, riveting and welding should be permitted only after thorough cleaning and testing of the tank with a combustible gas indicator to make sure that it is free of vapours and after a work permit has been issued by an authorized person. Purging shall be continued while repair work is in progress. In all cases, if repair work is interrupted, the tank atmosphere should be checked thoroughly and a new work permit issued before resumption of work.

11. WASTE DISPOSAL

11.1 All local and state regulations concerning waste disposal to streams, municipal treatment plants, or into the ground shall be determined and complied with.

11.2 Small quantities of methanol can be disposed of by pouring on dry sand or earth and then cautiously igniting it. The burning should be done in a remote area, safely away from buildings and other combustibles.

11.3 Waste mixtures containing methanol shall not be allowed to enter drains or sewers where there is a danger of vapour becoming ignited.

11.4 Large quantity of waste mixture can be disposed of by atomizing in a combustion chamber.

(*Continued from page* 2)

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Printed at Simco Printing Press, Delhi, India

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